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(30)Priority

Priority number : **363 653** Priority date : **13.01.1988** Priority country : **JP****(54) MATERIAL FOR EXTERNAL APPLICATION****(57)Abstract:**

PURPOSE: To obtain the subject material having air permeability and moisture permeability, excellent in the followability to the skin and reduced in a feeling of physical disorder such as a stretching feeling by using a porous plastic base material composed of a polyolefinic resin having specific tensile strength, elongation and modulus and specifying the moisture permeability of said base material when a pressure-sensitive adhesive layer is provided to the single surface of the base material.

CONSTITUTION: A material for external application is formed from a porous plastic base material composed of a polyolefinic resin having tensile strength of 100-500kg/cm², elongation of 50% or more and 25% modulus of 25-100kg/cm² and the moisture permeability thereof when a pressure-sensitive adhesive layer is provided to the single surface of the porous plastic base material is 300g/m².24hr or more. As the polyolefinic resin, a linear low density polyethylene resin is used especially desirably because of its excellent productivity and processability and low production cost. A filler is compounded with the polyolefinic resin if desired and, as the filler, calcium carbonate, talc, clay, bentonite or the like are designated and the average particle size of the filler is 30μm or smaller.

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[Title of the Invention] Externally Applicable Aids

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Specification

1. Title of the Invention Externally Applicable Aids

2. Scope of Claims

(1) An externally applicable aids which comprise porous plastic substrate made of polyolefine type resin, characterized by having 100 to 500 kg/cm of tensile strength, 50% or more of elongation, and 25 to 100 kg/cm² of 20% modulus, and the externally applicable aids shows 30.0 g/m² ·24hr or more of permeability, when a pressure-sensitive adhesive layer is provided on one side of said porous substrate.

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(2) The externally applicable aids according to Claim 1, wherein the porous plastic substrate is formed by extending sheet material, which comprises 100 wt parts polyolefine resin and 10 to 30 wt parts elastic composition of ethylene-propylene rubber, and 100 to 300 wt parts filing material..

(3) The externally applicable aids according to Claim 1 or 2, wherein the pressure-sensitive adhesive layer is of a copolymer, which comprises monomer of a copolymer containing carboxyl group, a monomer of acrylate or metacryate alkyl ester (having 1 to 14 carbon atoms), and a vinyl monomer which is capable of copolymerizing therewith, and having 50,000 or more in molecular weight, and 250 °K or lower in glass transition temperature.

3. Detailed Description of the Invention

(a) Field of the Invention

The present invention relates to an external application aids, which is used for applying on injury in medical field, which requires aeration and moisture protection. In particular, the present invention relates to first aids medical sheet, large scale medical sheet dressings and draping materials, which are formed by coating pressure-sensitive adhesives over porous plastic substrate.

(b) Prior Art

Hitherto, since an adhesive sheet, which is used for medical application, liable causes trouble on skin, if a sheet for use in medical aids is applied for a long term, the aids are required for humid and humor permeability in order to protect these troubles. Furthermore, aids are required for movability to smoothly follow movement at a joint of born.

Thus far a plastic film, such as polyurethane or polyvinylchloride, is conventionally used.

(c) Problems to be solved by the Invention

A polyurethane film is, however, expensive and extremely deteriorates in aeration and permeability, when a thickness of the sheet becomes large, thereby causing skin trouble. Accordingly, if a plastic film is used as an externally applicable aids, thickness thereof is required to be lower than 40 μm . But, the polyurethane film having such a thickness shows remarkably low strength and loses self suspension property, resulting in causing handling trouble.

Besides these, since polyurethane film itself does not inherently possess permeability, fine holes of the film is conventionally made with perforating machine to attain required aeration and permeation properties. However, the holes on the film,

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thus prepared, are widely spread having large distances, and aeration and permeation of the film are merely made through these holes. The rest of almost area in the film shows neither aeration nor permeation. Thus, the perforated film inherently has drawbacks to obtain homogeneous permeability through the film surface.

When the porous film with many small holes is formed by penetration, each size of the holes must become large, resulting in drawbacks due to permitting water and bacteria into the film.

According to the present invention is to provide the externally applicable aids, which has aeration and permeation throughout the whole surface, and shows excellent feelings on skin

(d) Means for solving the Problems

As the earnest study on the problems above due to the plastic porous substrate, the inventors of the present invention were succeeded to attain the present invention, which resides in using a specific porous plastic substrate, which is made of polyolefine resin as a substrate, and permeation of the aids being 300 g/m² 24hr or higher, when an adhesive layer is formed on one side of the substrate. The aids of the present invention shows excellent aeration and permeability having no trouble on the skin, and excellent following to the skin without feeling undesirable touch.

That is to say, according to the present invention the externally applicable aids comprise the porous plastic substrate, having tensile strength in 100 to 500 kg/cm², elongation in 50% or more, and 20% modulus in 25 to 100 kg/cm², and permeability of the externally applicable aids show 300 g/m² 24hr, when the aids provide the pressure-sensitive adhesive on one side of the substrate.

The present invention is further explained in more detailed.

An example of the polyolefine resin according to the present invention includes polyethylene resin, polypropylene resin, and ethylene-vinyl acetate copolymer resin. Among these, linear low density polyethylene resin is preferable due to excellent productivity and workability, and cheap material.

Said polyolefine resin may be used alone, or in combination with two more kind of resin, such as ethylene-vinyl acetate and the like. The porous plastic substrate may be prepared with one type, or two or more separate types thereof.

Among the polyolefine resins, a linear low density polyethylene resin is preferable in forming porous plastic substrate due to excellent productivity and workability and reasonable preparing cost.

Said linear low density polyethylene resin is a copolymer of ethylene and a-olefine, example of which includes butene, hexene, octene and the like.

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The above polyolefine resin optionally includes those, containing filler, on demand, example of which includes calcium carbonate, talc, clay, kaolin, silica, barium sulfate, kaolin sulfate, aluminum hydroxide, zinc oxide, calcium oxide, titanium oxide, alumina, mica, and bentonite.

An average diameter of the filler is 30 μm or smaller, preferably 0.1 to 1.0 μm . The larger the particles, the higher the permeability. Contrarily, if the particle size becomes smaller, the powder will cause coagulation to deteriorate dispersing property.

A mixing ratio of the above polyolefine resin (A) to filler (B) is desirably 100 parts by weight of (A) to 50 to 400 parts by weight of (B). Provide that (B) becomes too small, such as 50 wt parts or smaller, aeration and permeation properties become worse to cause wet skin, thereby making skin whitened, and reliably occurring stimulation for skin. On the other hand, when the ratio of (B) becomes over 400 weight parts, mixing and molding properties become worse, property of the film becomes also lowered. Thus, the mixing ratio of (B) is desired to be 10 to 300 weight parts with respect to 100 weight parts (A).

The porous plastic substrate may be made by using with the above polyolefine resin, and a method for making the same is as follows

Examples of the polyolefine sheet include, those of polyolefine resin being directly formed by stretching in one or double axis stretching machine; porous substrate being obtained by stretching, thereafter eluting soluble filler or organic material with acid or alkali solution; those obtained by mixing polyolefine resin and solvent ,forming sheet, and evaporating the solvent, and the like.

Under the circumstances, forming of the polyolefine sheet may be carried out using conventional molding apparatus and method, and inflation forming machine and T-die forming machine are preferably used. The sheet, thus obtained, is stretched with single or double axis molding machine to form porous plastic substrate. These stretchiness may also be conventionally made with conventional machine, such as roll stretching machine, simultaneous double axis stretching, consecutive double axis stretching, etc.

Among the porous plastic substrate, since those obtained by solvent method is considered to be undesirable due to attack skin with remained solvent, those made by stretching method are preferable.

Sheet forming is in accordance with a best process, either in extruding or inflation, to be a thickness of 50 to 1000 μm . It is necessary to make porous substrate by stretching 5-fold or lower, preferably 1.1 to 3.5 fold, with one or double axis machine under 100 to 500 kg/cm^2 in tensile strength, under a melting point of the polyolefine

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resin or lower, preferably 15 to 30 °C lower than the melting point.

In the case of stretching method, when the stretching rate is lower than 1.1, the stretched part and unstretched part are existed in the product sheet, which is ununiform. On the other hand, when the stretching rate is over 5-fold, a broken part is appeared undesirably.

According to the present invention, the stretching rate means a length and width of the sheet after stretching in terms of those in original sheet.

The porous plastic substrate of the present invention may be heat treated to stabilize the dimension, and to obtain homogeneous sheet and those having uniform aeration and humid permeation properties, after stretching in one or double axis direction. For example, if the polyolefine sheet is stretched 4-fold first, and is heat treated to make stretching rate to 2-fold, the stretched sheet thus obtained shows more uniform than those obtained by originally stretching into 2-fold.

Besides the above, a surface of the porous plastic substrate may be applied with corona treatment to enhance anchoring effect with pressure-sensitive adhesive material, stated herein after. The porous plastic substrate may contain a heat stabilizing agent, UV stabilizer, pigments, and the like, on demand.

The porous plastic substrate according to the present invention has a softness to follow skin surface, and is required to design so as to neglect foreign feeling on skin, when the product is applied, and so as to be smoothly followed with born bending.

In other words, a required property for the externally applicable aids is to be tightly adhered to skin, as well as followed to movement of skin in the born surface, when it is applied on the bending part and surface over born position. Accordingly, the aids attached on the human skin can not follow deformation due to shrink of the skin. If elasticity of the porous substrate becomes much lowered, mechanical stimulation, such as expansion, on the skin is occurred, and the substrate becomes easily apart from the skin. The porous plastic substrate of the present invention is desired to provide suitable elasticity. A method for providing the certain amount of elasticity to the porous plastic substrate includes an addition of low melting polymer, rubber materials, and plasticizer. According to the present invention, ethylene-propylene type rubber composition, such as EPR, EPT, and the like, is preferably added in order to give the aids having excellent followability to the skin and having less stiffness on the skin.

The ethylene-propylene type rubber elastic composition is not specifically restricted, provided that the rubber composition has 5000 to 30000 in number average

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molecular weight, and example thereof includes cyclic or non-cyclic copolymer having ethylene olefin and conjugated or non-conjugated double bonds(hereinafter referred to as EPDM)..

Example of EPDM includes ter-polymer, comprising ethylene propylene or butene-1 and polyethylene monomer, which is disclosed hereunder. Example of said polyethylene monomer includes dicyclopentadiene, 1,5-cyclooctadiene, 1,1-cyclooctadiene, 1,6-cyclododecadiene, 1,7-cyclododecadiene, 1,5,9-cyclododecatriene, 1,4-cycloheptadiene, 1,4-cyclohexadiene, 1,6-heptadiene, norbornadiene, methylene norbornene, ethylidene norbornene, ethylidene norbornene, 2-methylpentadiene-1,4, 1,5-hexadiene, methyl-tetrahydroindene, 1,4-hexadiene, etc.

Polymer proportion of each monomer preferably comprises 30 to 80 mol% in ethylene, 0.1 to 20 mol% in polyethylene, and remainder in olefin, and is terpolymer preferably having Mooney viscosity of 1 to 60

A proportion of ethylene-propylene type rubber composition(C) to polyolefine type resin(A) is 100 weight parts of (A) to 5 to 150 weight parts of (C), most preferably 10 to 30 weight parts of (C)

In the above mixing ratio, when amount of (C) is less than 5 weight parts, the polymer base does not possess sufficient elasticity to follow the shrinkage of the skin. Contrarily, when the amount of C is over 150 weight parts, a mixing property of the composition becomes worse thereby causing uneven surface of the sheet. The both compositions above are undesired.

The porous plastic base according to the present invention is desired, since the base, which is formed by stretching sheet type compound, comprising 100 weight parts of the polyolefine, 10 to 80 weight parts of ethylene-propylene type rubber composition and 100 to 300 weight parts of filler, shows more excellent air and humid permeability, as well as shows excellent property in following to a movement of the skin.

When said porous plastic base has 100 to 500 kg/cm² of tensile strength, 50 % or more of elongation, and 25 to 100 kg/ cm² of 20 % modulus, it is liable to easily follow to the movement of the skin. On the other hand, when the base has 500 kg/cm² or higher of the tensile strength, less than 50 % of elongation, and 100 kg/ cm² or higher of 20 % modulus, it is not desired to give unconformable feeling and mechanical stitch on the skin, since the base can not be followed to the movement of the skin due to excessively higher rigid in the composition. Similarly, when the base shows less than 100 kg/cm² of tensile strength, and less than 25 kg/ cm² of 20 % modulus, it is also not desired, since the base will become too soft to cause handling troubles, such as inconvenient workability.

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In the present invention, an example of pressure-sensitive adhesive layer, which is applied over one side of the porous plastic base, includes natural rubber layer, and a various pressure-sensitive resin layers, such as of polyisoprene type, polyvinyl ether type, polyacrylic acid ester and the like.

The pressure-sensitive adhesive layer according to the present invention is desired as those having properties in less stimulation on the skin, excellent adhesion, and high permeability for air and moisture. In view of the above characteristics, a copolymer of acrylic acid or methacrylic acid alkyl ester monomer and a polymeric monomer containing carboxyl group is preferred.

A reason for using a monomer (D) of acrylic acid or methacrylic acid alkyl ester resides in said component providing no stimulation on the skin, and excellent permeability and less deterioration in adhesives.

Besides these, when a compound, in which a monomer (D) of acrylic acid or methacrylic acid alkyl ester is copolymerized with a polymerizable monomer (E) containing carboxylic group, is used, the porous polymer base shows adequate anchoring properties for adhering thereof to the skin, and does not cause so-called "remaining" trouble. Contrarily, the composition, exclusively containing the monomer (D), in other words, without copolymerizing with the monomer (E), has less adhesion.

The copolymer is preferably has 250°K, preferably 180 to 250°K of glass transition temperature, and 50,000 or more, preferably 500,000 to 2,000,000 of weight average molecular weight.

If the glass transition temperature becomes over 250°K, adequate adhesion and coagulation force are not obtained. Similarly, if the weight average molecular weight becomes less than 50,000, adequate adhesion and coagulation force are not obtained. Further, said copolymer is more practically preferred, in using the later (E) within a range of 1 to 10 weight parts related to 100 weight parts of the former (D).

In the above mixing ratio of the composition, when the monomer (E) has less than 1 weight %, a coagulation force becomes rather weak, and when the (E) has higher than 10 weight %, the stimulation on the skin appears on applying the base, due to unnecessarily higher coagulation because of the introduction of the polar group.

A thickness of the pressure-sensitive layer is desired to be in 10 to 60 μm . When the thickness is less than 10 μm , a sufficient adhesion on the skin is relatively low, contrarily, when the thickness is over 60 μm , a sufficient permeability of the base can not be attained, even if the above copolymer is used. Thus, 10 to 60 μm thickness of the pressure-sensitive layer is required for obtaining excellent adhesion and permeability.

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An example of the acrylic or methacrylic acid alkyl ester monomer of the copolymer includes ethylacrylate, propylacrylate, butylacrylate, iso octylacrylate, isononylacrylate, decylacrylate laurylacrylate, or, methacrylic acid ester thereof. These may be alone or in two or more combination.

An example of the polymeric monomer containing carboxyl group includes acrylic acid, itaconic acid, maleic acid, and the like. With the above copolymer mixture, vinyl monomer may be used, on demand. In the process for preparing the pressure-sensitive adhesives, conventional polymerizing catalysts, such as azobis compound, peroxy compound, may be used.

As for polymerization process, any polymerization, such as solvent polymerization, emulsion polymerization, suspension polymerization, etc., may be used.

For example, a polymerization is made by adding a monomer mixture of acrylic acid, acrylic acid alkyl ester monomer, and above copolymerizable vinyl monomer, into a reaction vessel with a solvent, such as ethylacetate, and radical generating catalyst. The polymerization is completed in 10 to 20 hours.

The porous plastic base made of the above mentioned polyolefine resin and pressure-sensitive adhesive layer are integrated into a layer, which desirably shows $2300 \text{ g/m}^2 \cdot 24\text{hr}$ or more of moisture permeability, preferably 300 to $2000 \text{ g/m}^2 \cdot 24\text{hr}$.

An amount of perspiration from human skin is differed depending on a individual condition, and a part of the skin. If the moisture permeation rate is less than $300 \text{ g/m}^2 \cdot 24\text{hr}$, a part of the skin occurring more perspiration is hard for sufficient amount of permeating, resulting in causing dumpy and skin trouble.

The permeation rate according to the present invention is measured by the following method.

Sample of externally applicable aids, having 50 mm in diameter, is set over an opening of a glass vessel, having 38 cm in diameter, and 40mm in height, which is filled with 10 ml of distilled water, so that the surface of the pressure-sensitive layer may be faced towards the water, and is fixed, followed by sealing. Then, the vessel holds stand still in a chamber for 24 hrs, which maintains. At 40°C of temperature, and under 30 % of relative humidity.

After that, an amount of the water in the glass vessel is measured to obtain an liberated amount. A permeation is calculated as $\text{g/m}^2 \cdot 24\text{hr}$.

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The externally applicable aids according to the present invention is prepared by directly coating the pressure-sensitive adhesive layer onto the porous plastic substrate of polyolefine resin, and drying thereof to obtain the product. A separate sheet (paper) may be covered over the exposed surface of the pressure-sensitive layer. Alternatively, the pressure-sensitive adhesive is coated over the separate sheet (paper) and is dried, and subsequently the porous plastic substrate is integrated with the pressure-sensitive layer to form the aids with the separating sheet. Thus, the aids according to the present invention, which is protected with separate sheet, is obtained.

(e) Function

The externally applicable aids of the present invention has the constitution disclosed above, which comprise specific porous plastic base of polyolefine resin, having properties in 100 to 500 kg/cm² of tensile strength, 50 % or more of leongation, and 25 to 100 kg/cm² of 20 % modulus, and pressure-sensitive adhesive layer, which is provide on one side of the porous plastic base. Since the permeability of the porous plastic base, on one side of which the specific pressure-sensitive adhesive layer is provided, shows 300 g/m², the aids of the present invention has no problem on the skin, such as permeability, itches, and the like. Accordingly, the aids of the present invention has excellent function without show unpleasant feelings, even though the aids has excellent attachment over the skin with following movement of the skin.

(f) Examples

The present invention will be explained in detailed with referring to the examples, which do not construe to limit thereof. In the examples, terms of parts and percents mean in weight.

(i) Preparation of linear low density porous polyethylene plastic base (I to VI)

A mixture composed of linear low density polyethylene resin (MI 2.0, density 0.93), EPDM(trade name BPT 9720, manufactured by Mitsui Petroleum Chemistry, LTD) as a rubber like material, calcium carbonate(average particle size 2 µm, treated with aliphatic acid) as a filler, and stearic acid as a lubricant, in each amounts, stated in the

	Polymer	Filler	Rubber	Lubricant	
Base I	100	125	40	1.5	100
Base II	100	150	40	1.5	103
Base III	100	150	40	1.5	92
Base IV	100	200	40	1.5	114
Base V	100	200	20	1.5	88
Base VI	100	250	20	1.5	96
Base VII	100	200	40	1.5	80

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Table 1 below, were mixed and fully kneaded in double axes blender(TEM-50, made by Toshiba Machine Co.). The mixture, blended, was formed into pellets in a conventional manner.

The product, thus obtained, was melted and formed into a film by inflation extruder having dies of 65 mm in diameter, to obtain films having thickness disclosed in the Table 1.

The film, thus prepared, was stretched with roll stretching machine, in a manner of one axe stretching method(I to VI) or subsequently double axes method, to form the porous plastic base having stretched rate, stated in the Table 1.

The stretching conditions were at 60 °C of stretching temperature, and 6 m/min of stretching speed. The stretching rate was controlled by adjusting speed of roll, so that the film may have value stated in the Table 1.

Characteristics of the porous plastics base are shown in the Table 1.

	Polymer	Filler	Rubber	Lubricant	
Base I	100	125	40	1.5	100
Base II	100	150	40	1.5	103
Base III	100	150	40	1.5	92
Base IV	100	200	40	1.5	114
Base V	100	200	20	1.5	88
Base VI	100	250	20	1.5	96
Base VII	100	200	40	1.5	80

	Stretching rate	Tensile Strength (MD) kg/cm ²	Elongation (MD) Note 1)	20% Modulus (MD) kg/cm ² Note 1)	Humid Permeation G/m ² /24hr Note 2)
Base I	4	264	68	83	800
Base II	3	204	230	64	1600
Base III	4	217	154	66	2000
Base IV	4	179	126	62	3400
Base V	4	184	86	59	3200
Base VI	4	152	82	54	3600
Base VII	Vertical 2.0 Lateral 1.4	163	120		3800

Note 1) A method for measurement for the elongation(MD) and 20% modulus (MD) stated in the Table 1 is as follows.

The elongation of the base sample, having 100 mm in lateral, and 20 mm in vertical, was held at both side with 50 mm in distance, and pulled thereof in 300 mm/min speed along S-S line with a tension meter (Tension VTM-III L, made by Orientic Co.) The elongation(%) means those, when the sample was cut, and 20 %

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modulus means a strength at 20% stretched time.

Note 2) The moisture permeation, listed in the Table 1, was measured as follows.

A 10 ml of distilled water was charged in a glass vessel, having 30 mm in inside diameter, and 40mm in height, and sample aids 50 mm in thickness, was covered over the open end of the vessel. A pressure-sensitive face of the aids was faced to down wards.

Next, the vessel, having the sample aids on the top, was set in a chamber maintaining constant humid and temperature, and stand still at a temperature of 40°C, and 30% of relative humidity, for 24 hours. Thereafter, an amount of the water, evaporated, was measured, and identified as humid permeability under g/m²/24hour.

(m) Preparation of pressure-sensitive layer(A)